Generation of Surface Excitations on Dielectric Spheres by an External Electron Beam

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The energy loss and differential probability of energy losses is calculated to all multipole orders for a charged particle moved uniformly past a sphere. The sphere's response is characterized by use of a local dielectric function.

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A particle approaching a polarizable body may engender collective excitations which act back upon the particle. Both virtual and real excitations occur, and the resulting interation thereby has both conservative and dissipative components. Excitations may include surface plasmons,[1] surface optical phonons,[2] surface excitons, helicons, ripplons,[3] and other collective effects including, for example, orientation of permanent molecular dipoles.[4] Similar effects may be found in atomic and nuclear physics (as in Coulomb excitations of nuclei). For the case of a plane-bounded medium, a large body of literature exists[1, 2, 5]; while for the case of a spherically symmetric body, the literature is somewhat less extensive.[6]

Because of its general applicability, the case of a point charge moving past a spherically symmetric, polarizable body has not only been of continuing interest in fundamental physics, but also has attracted interest from fields such as materials science and electronics. The advent of modern scanning-transmission electron microscopes (STEM) has allowed probing of nanometer-sized bodies with a 0.2-nm beam of electrons. Energy analysis of the transmitted beam has been accomplished in this case.[7, 8] In other experiments, the radiative decay of Coulomb-stimulated surface plasmons has been used to diagnose the spectrum of energy losses.[9]

Despite the general and high level of interest in the problem, the formulation of the energy-loss probability for a charged particle passing near a general dielectric polarizable sphere is unsatisfactory to date. In particular, for ever closer trajectories one expects ever higher contributions from higher multipoles, since one tends toward the planar limit. The calculations for the dipole modes are quite straightforward, but little work has been done in the general case. The well-known solution of electrodynamics for the case of a uniformly moving charge and a harmonically bound charge[10] is the equivalent of the dipole approximation used for a sphere. Schmeits,[11] for example, has considered the dipole and linear quadrupole excitations, but higher multipoles, including the polar and the azimuthal indices, are equally important in most experiments. The classical theory of impact-parameter-dependent energy losses for planar interfaces has been shown[8] to account for some of the observations on small spheres of oxide-coated Al and of silver. Wheatley, Howie, and McMullan[8] used the planar results for spheres by replacing the impact parameter with respect to the sphere by the instantaneous value at each point of the track and resolving the force in the track direction. While this *ad hoc* procedure is easy to apply and might provide useful results, clearly one needs a more comprehensive approach which yields a good understanding of the energy-loss process. Kohl[12] has examined, for the dipole mode, the validity of the classical theory for such a highly focused beam. Ritchie and also Ritchie and Howie[13] have analyzed the surface-plasmon dipole mode and the validity of the classical theory of the incident beam in STEM experiments. These experiments offer a direct test of the classical theory of energy loss, but the comparison requires the inclusion of all angular-momentum states because of the proximity of the beam to the target when the interaction is of sufficient strength to yield the necessary signal-to-noise ratio. Barberan and Bausells[14] have used a free-electron gas model and a numerical technique to assess the energy-loss probability in this case, but clearly one needs a more general approach which yields a wider range of applicability for the case of an arbitrary frequency-dependent dielectric function.

In this paper we derive the energy-loss probability for a point charge moving uniformly past a sphere with a local, but otherwise arbitrary, dielectric function $\epsilon(\omega)$ where ω is the angular frequency. All multipolar contributions are included. The sphere is assumed to be sufficiently small that electrodynamic retardation may be neglected. For a free-electron gas, a comprehensive result is also derived in the occupation-number representation in terms of the coherent states of the plasmon field excited by the fast particle.

The total energy loss W may be written in terms of a probability function $P_\omega(a,b,v)$,

$$W=\int_0^\infty P_\omega(a,b,v)\omega\,d\omega, \tag{1}$$

where b is the distance of the charge q from the center of the sphere of radius $a<b$ at closest approach. Here v is the velocity of the charged particle.

To obtain $P_\omega(b)$ we solve Poisson's equation, match boundary conditions with the Fourier components of the fields, and obtain the field due to the induced excitations. This field is then used to evaluate the energy loss. A detailed exposition of the rather lengthy and the tedious work involved is to be presented in a later paper. We find, in Hartree atomic units ($e=\hbar=m=1$), that for a sphere of radius a and for a charge q at distance $b>a$ from the center of the sphere (at closest approach), one has

$$P_\omega(a,b,v)=\frac{4q^2}{\pi v^2a^2}\sum_{l=0}^{\infty}\sum_{m=0}^{l}A_{lm}\left(\frac{\omega a}{v}\right)^{2l}K_m^2\left(\frac{\omega b}{v}\right)\mathrm{Im}[\alpha_l(\omega)], \tag{2}$$

where v is the charge's speed, while

$$\alpha_l(\omega)=\frac{\epsilon(\omega)-1}{\epsilon(\omega)+(l+1)/l}a^3 \tag{3}$$

and

$$A_{lm}=(2-\delta_{0m})/(l+m)!(l-m)!. \tag{4}$$

Here δ_{0m} is the Kronecker delta, and K_m is the modified Bessel function of order m. For $l=1$ the dipole contribution goes over into the usual result; in this case the energy loss is proportional to the square of the ω Fourier component of the external field if it is taken to be constant over the volume of the sphere. The usual result for a harmonically bound charge replacing the sphere is obtained when one takes a unit volume containing a single charge replacing the sphere and if $\epsilon(\omega)$ is taken to be descriptive of such a situation.

Equations (2) and (3) can be used for any dielectric function; in particular, when $\epsilon(\omega)=1-\omega_p^2/\omega^2$, we have the free-electron gas result.

The above results can be obtained by use of a coherent-state type of approach[2,15] in a second-quantization formulation, where the particle–surface-modes interaction Hamiltonian is written as

$$H_I=\sum_{lmp}\Gamma_{lmp}(t)(b_{lmp}+b_{lmp}^\dagger), \tag{5}$$

where $\Gamma_{lmp}(t)$ is given by[11,14,16]

$$\Gamma_{lmp}(t)=\gamma_l(a)(a/r)^{l+1}\Theta(r-a)+(r/a)^l\Theta(a-r)\,Y_{lmp}(\theta,\phi), \tag{6}$$

and where

$$\gamma_l(a)-(\omega_p^2/8\pi\omega_l)^{1/2}4\pi(l/a)^{1/2}(2l+1)^{-1}. \tag{7}$$

Here $\omega_l=(\omega_p^2l/2l+1)^{1/2}$ and Θ is the Heaviside step function, while $r^2=b^2+v^2t^2$. The Y_{lmp} are the real spherical harmonics.[17,18] The wave function of the surface modes can be solved exactly[2,15] in the interaction picture and is given by [$L=(lmp)$]

$$|\psi(t)\rangle=\prod_L\exp[-|\alpha_L(t)|^2]\exp(\alpha_Lb_L^\dagger)\exp(-\alpha_L^*b_L)|\psi_I(-\infty)\rangle. \tag{8}$$

Here $|\psi(-\infty)\rangle$ is the plasmon-field vacuum state, and

$$\alpha_L(t)=-i\int_{-\infty}^{t}\Gamma_L(t_1)\exp(i\omega_lt_1)dt_1. \tag{9}$$

The probability that a mode L, with energy ω_l, will have been excited at time t is then

$$P_L(t)=|\alpha(t)|^2. \tag{10}$$

The total energy loss after the incident particle has passed from $t=-\infty$ to $t=+\infty$ is

$$W=\sum_l P_{\omega_l}(a,b,v)\omega_l, \tag{11}$$

where $P_{\omega_l}(a,b,v)=P_L(\infty)$; and after some algebra we get

$$P_{\omega_l}(a,b,v)=\frac{2a}{v^2}\sum_{l=0}^{\infty}\sum_{m=0}^{l}A_{lm}\omega_l\left(\frac{\omega_la}{v}\right)^{2l}K_m^2\left(\frac{\omega_lb}{v}\right). \tag{12}$$

Expression (12) agrees, of course, with (2) when one substitutes in (2) the $\epsilon(\omega)$ for free-electron gas. Equations (2) and (12) allow us to understand the relative importance of a given mode in the loss process. When $\omega a/v\ll1$, the $l=1$ term dominates, and we regain the dipole approximation. If b is near in size to a, the dominant contribution to each l comes from the $m=l$ term; if $\omega a/v\ll1$ but $\omega b/v\gg1$, no m term prevails, and $P_\omega(b)$ goes like $(\omega a/v)^{2l}$. If $\omega a/v$ is greater than unity, many l's are necessary. Moreover, under the same conditions of energy, sphere radius, and impact parameter, different modes might be necessary to understand different materials, because the relevant ω's involved would vary. We have carried out a detailed study of these points for several materials using both a free-electron gas model and experi-

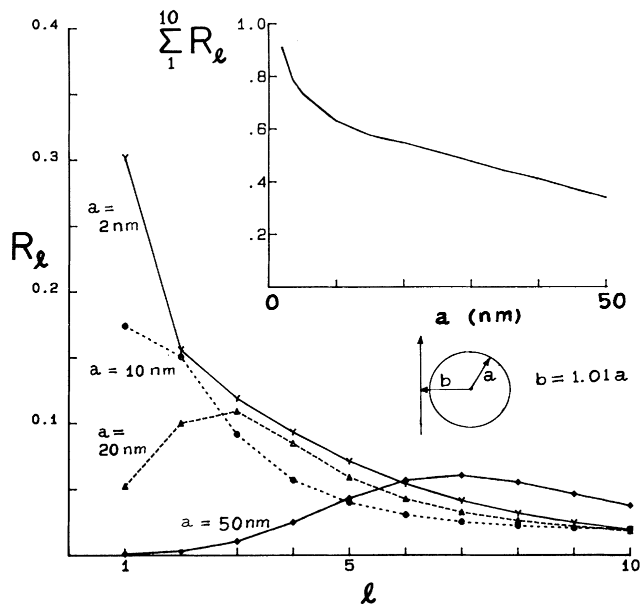

FIG. 1. Relative weight R_l of the lth-mode contribution to the total energy loss. [Calculated in the free-electron gas model for $r_s = 2$ as a function of the mode number for an electron of energy 50 keV at grazing incidence ($b \approx a$) for different sphere radii.] Also, the contribution to the loss of the first ten l modes is shown as a function of the radius of the sphere.

mentally measured values of $\epsilon(\omega)$. A complete report of our work will be published elsewhere; but to illustrate our point, we show in Fig. 1 for a grazing-incidence electron of energy 50 keV the relative weight of the contribution to the total energy loss of the lth mode in the free-electron gas model for a one-electron radius of $r_s = 2$ for different sphere radii. As shown, for large enough radii, the dipole contribution is negligible. Also, we show on the right-hand side the relative contributions of the first ten l modes as functions of the sphere radius.

In Fig. 2 we show the probability of losing energy ω for a 50-keV electron at grazing incidence on a sphere of radius $a = 10$ nm. We show the contributions of the dipole mode, the first two l's, and ten l's, and the total probability. For small radii and low energy losses, the dipole contribution dominates; while even at small radius, it is inadequate to describe the high energy losses. We have used experimental optical data for $\epsilon(\omega)$ in the calculations.[19]

In conclusion, we have presented a useful, simple way of calculating all the multipole contributions to the energy-loss probability for electrons interacting with dielectric spheres which could be most useful in a number of different problems, as described above. For a large number of experimental situations, many multipoles should be included, since theories based on the

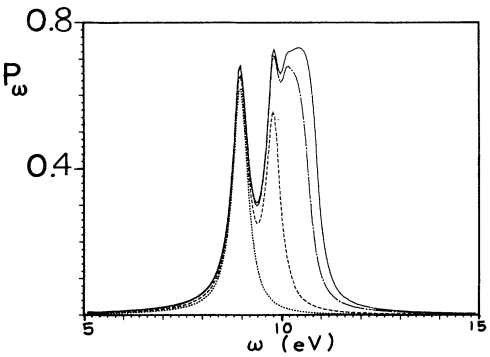

FIG. 2. Probability P_ω of losing energy ω for a 50-keV electron moving at grazing incidence on an aluminum sphere of radius $a = 10$ nm.

dipole approximation could lead to serious error in analysis of the experimental data. Similar considerations apply to voids.[20]

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